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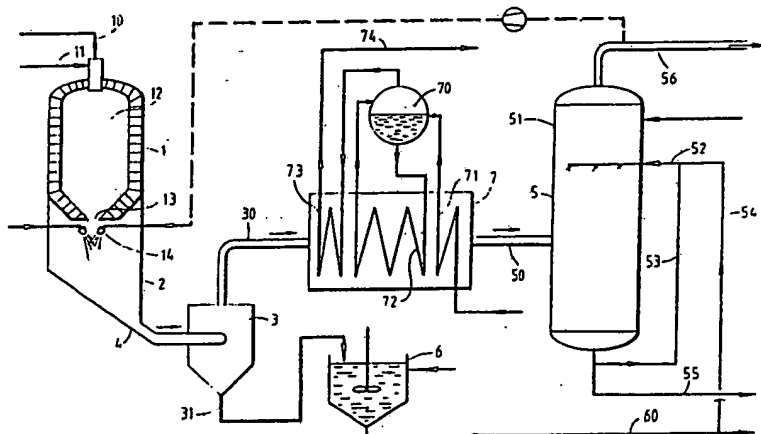
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chemical particles is led from a cooling chamber (2) arranged in connection with the gasification reactor (1) to a separating arrangement (3), preferably a cyclone, where the non-adhesive chemical particles are separated from the gas, the gas stream, essentially cleaned of chemical particles, is taken out via an upper connection on the separating arrangement (3) while the chemical particles are taken out via a lower connection on the separating arrangement (3), wherein the melt particles leaving the reactor in the gas mixture are cooled to a temperature where they have at least partially solidified and been converted to solid phase, so that the particles included in the gas mixture are non-adhesive, and that a subsequent heat exchange of the separated gas is carried out from an essentially preserved temperature level.



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5 Title:

Method for recovery of chemicals and energy
from spent liquor.

Technical background:

10 The present invention relates to a
process for the extraction of chemicals and energy from
cellulose spent liquors, primarily for the extraction of
chemicals and energy from the gas stream from a reactor
for black liquor gasification.

15

State of the art:

Nowadays ever stronger demands are
being made, in relation to different types of process,
for recovering substances that are integral to the
20 process, which substances can be reusable chemicals and
also energy which has been added or liberated during the
process. These demands have mainly arisen with regard to
the environment and for economic reasons. A general
problem is that in certain processes gas mixtures are
25 obtained that contain both melt and gas phase, which gas
mixtures are difficult to deal with in regard to the
recovery of the content of chemicals and energy. In
particular it is the melt particles that cause problems,
since these, in an associated heat exchange process,
30 often settle on the convection surfaces of the heat
exchanger, something which is undesirable. This problem
arises during use of the known process according to
SE-B-328 179.

An industrial process area where
35 problems of this nature arise is in connection with the
gasification of spent liquors from paper pulp production.
The gasification of spent liquor takes place in a
reactor, where the content of organic substances in the
spent liquor is pyrolysed and partially incinerated so
40 that heat energy can be extracted and the chemical
content separated off for recovery. The invention will be

described below in relation to the gasification of black liquor, in order to describe the invention in more concrete fashion, which does not, however, limit the invention to this specific area.

5 Black liquor is obtained as a residual product, spent liquor, in the production of pulp according to the sulphate cellulose method. The black liquor contains alkaline chemicals, in the form of various sodium compounds, which it is desirable to
10 recover for reuse in the pulp production process. The recovery process comprises a heating stage, a reactor, where the organic molecular chains are broken down by pyrolysis and incineration to energy-rich gas and the inorganic content mainly forms finely divided particles
15 of chemical melt which can be recovered. The pyrolysis in combination with the incineration thus liberates heat energy, usually the temperature is about 1000°C in the reactor, and produces a combustible gas. It is desirable to extract the liberated heat and also exploit the
20 combustible gas by means of further incineration.

 SE-B-448 173 describes a method for the recovery of chemicals and energy from black liquor. According to SE-B-448 173 it has been possible to recover the sensible heat in the gas and simultaneously avoid
25 settling problems by means of directly allowing the gases to pass through a liquid bath. Besides the melt particles being taken up by the said liquid, which is green liquor, the gas is simultaneously cooled. The gas which leaves the liquid bath and which has been freed from melt
30 particles thereby achieves a temperature which in an unpressurised system only amounts to the order of 80°-90°C, which also corresponds to the approximate temperature in the green liquor bath. Thus, in this unpressurised system, a melt-free gas flow is obtained at
35 about 90°C, as is a liquid bath, consisting of green liquor, at about 90°C. Even if the process according to SE-B-448 173 is carried out at as high a pressure as

150 bar, heat recovery can at best take place by the generation of 300°C saturated steam.

From the energy recovery point of view these temperatures are too low to be optimal. It is therefore desirable to be able to transfer the heat at a higher temperature level so that it can be obtained in the form of superheated steam, preferably for turbine operation with a view to producing electrical current. In operating steam turbines the highest degree of efficiency is obtained when the superheated steam is delivered at high pressure and high temperature, for example 150 bar and 600°C. Thus it is desirable to achieve heat exchange at as high a temperature as possible.

In the method described above, however, the gas is cooled down to a temperature in the region of 100-300°C, which limits the possibility for efficient energy recovery. It is evident from the above reasoning that it would be desirable to be able to extract the heat at a higher temperature, so that it can be recovered in the form of superheated steam.

A process is previously known from SE-B-182 336 for the extraction of chemicals and energy from cellulose spent liquors, preferably black liquor obtained in the sulphate cellulose process, wherein the spent liquor is conducted into a gasification reactor (1) for pyrolysis and partial incineration, wherein an energy-rich gas is formed containing particles of inorganic chemical melt, the said gas mixture is conveyed out of the reactor (1) and is thereby cooled by injection of a finely-divided cooling medium (cold gas), in connection with departure from the reactor (1), the said mixture of gas and non-adhesive chemical particles is conducted from a cooling chamber (2), arranged in connection with the gasification reactor (1), where they have at least partially solidified and been transformed into solid phase, so that the particles included in the gas mixture become non-adhesive, and thence to a

separating arrangement (3), preferably a cyclone, where the non-adhesive chemical particles are separated from the gas, the gas stream, which has been essentially cleaned of chemical particles, is removed via an upper connection on the separating arrangement (3) while the chemical particles are removed via a lower connection on the separating arrangement (3), and wherein a subsequent heat exchange of the separated gas is performed from an essentially preserved temperature level. This known method suffers, however, from certain operational and technical disadvantages. This is in particular the case if the generated gas is to be used for gas turbine operation since the known method does not provide sufficient purity for the operation of a combustion turbine. Furthermore the method lacks a well thought out use of the cooling medium or the scrubber medium, which makes the process difficult to optimise.

Solution and advantages:

A first object of the invention is thus to offer a process and an arrangement whereby it is possible to make use of the heat from a gas stream containing both melt particles and gas, without drastically lowering the temperature level of the gas before the heat exchange takes place, at the same time as settling problems are avoided. An additional object of the invention is to solve this in an optimal manner, in connection with application to gas turbines and in relation to the use of a cooling or scrubbing medium.

The abovementioned objects are achieved by the melt particles, which leave the reactor in the gas mixture, being cooled to a temperature not exceeding 700°C and the said finely-divided cooling medium being composed of water, together with the gas being washed after the heat exchange by being conducted through a washing arrangement (5), a so-called wet scrubber (5), for the washing out of remaining chemicals

in solid form and gas form and by the separated solidified melt particles, which are removed at the bottom (31) of the separating arrangement (3), being conducted to a receptacle (6) in which the particles are dissolved, wherein at least parts of the alkaline solution formed in this way are exploited for washing the gas in the said wet scrubber (5).

The abovementioned objects are achieved in an even more preferred manner with the aid of a process according to the invention for extracting chemicals and energy from black liquor obtained in the sulphate cellulose process, wherein the spent liquor is conducted into a gasification reactor for pyrolysis and partial incineration, so that a gas is formed that contains melt inorganic chemicals, the said gas is conveyed out of the reactor and is cooled by injection of finely-divided water to a temperature in the region of 500-700°C in connection with departure from the reactor, the said inorganic chemical content is cooled thereby at the same time to a temperature below its solidification point, gas and solidified melt drops are led to a separating arrangement, preferably a cyclone, where the chemical particles are separated from the gas and the gas stream, largely cleaned of inorganic chemical particles, is removed in an upper connection in order to be cooled in a waste heat boiler with generation of superheated high-pressure steam, and the chemical particles, separated off in the separating device, are dissolved in water, whereby so-called green liquor is formed.

It is true that it is previously known through SE-B-363 651 that the temperature of the gas and chemical melt that has been obtained can be decreased by spraying on water in the cooling section of the reactor. However, this document misleads the expert, since in this case cooling takes place down to 200°C before separation occurs. This low temperature is, as has already been indicated, undesirable from the point of view of heat

recovery.

Description of the figure:

5 The invention will be described in more detail below with reference to the attached figure in which is shown a basic assembly of the equipment for a procedure for carrying out the process according to the invention.

10 Thus a reactor 1 is shown to which is conducted black liquor via a first conduit 10 and air via a second conduit 11. In the reactor space 12 the black liquor is gasified by pyrolysis and partial incineration and thereby forms a gas/melt mixture, where the melt drops are present in finely suspended form, at a tempera-
15 ture of about 1000°C. Because the gasification takes place by means of substoichiometric supply of oxygen, a number of combustible gases are formed such as H₂, CO, CH₄, etc. The melt particles contain mainly Na₂CO₃ and NaS. At the reactor end comprising the reactor outlet 13
20 a cooling chamber 2 is arranged inside which are distributed a number of spray nozzles 14 which are fed with water and/or cooled gas via conduits 15. With the aid of the nozzles 14 the water and/or gas is finely divided and comes into contact with the hot exhaust gases from the
25 reactor 1. Thereby the exhaust gases are cooled to a temperature of about 650°C. This cooling results in the melt particles being converted into solid phase and thereby becoming non-adhesive. From the cooling chamber 2, which is located in connection with the reactor 1, the
30 gas is conducted with its content of solidified chemical particles onwards through a conduit 4 which leads to a cyclone separator 3.

35 In the cyclone separator 3 the solid and non-adhesive particles are separated from the gas and the gas leaves the cyclone via an upper conduit 30 while the crystalline particles are taken out through a lower conduit 31. The gas phase in the conduit 30 still retains

a temperature of about 650°C and is conducted in direct connection thereto into a heat exchanger unit 7 for the generation of superheated steam. Due to the purity of the gas, heat exchange can now take place without interfering deposition on the convection surfaces in the heat exchanger. The heat exchanger unit 7 comprises preferably a steam dome 70, a first heat exchanger core 71 for feed water which leads to the steam dome 70, a second coil 72 for production of saturated steam which leads back to the steam dome 70 and a third heat exchanger core 73 for generation of superheated steam, with a temperature of 300-600°C and a pressure of 20-150 bar, which is taken out via a conduit 74, preferably for the generation of electrical energy in a steam turbine according to the back pressure or condensing procedure.

After having passed through the heat exchanger unit 7 the gas has a temperature of about 200°C and is led via a further conduit 50 into a washing arrangement 5 for a final wash of the gas. This washing arrangement comprises a cylindrical casing 51 to which at a first level 52 is brought an alkaline solution by means of the spray nozzles in order to eliminate remaining chemicals from the gas, primarily H_2S . This alkaline solution can be obtained partly via a recirculating conduit 53 and partly from a receptacle 6. In the preferred case this receptacle 6 contains green liquor which has been prepared by dissolving the chemicals that were separated off in the cyclone 3 in water or so-called weak liquor. This green liquor has thus been obtained by dissolution of the chemical particles that were recovered from the separator 3. The liquor from the last-named receptacle 6 like that from the washer 5 is led away in conduits 60 and 55 for collection in receptacles (not shown) and for further processing in a causticisation stage for the production of white liquor which is reused in the digestion process.

The gas which is led away via a

conduit 56 at the top of the gas washer 5 is exploited for the production of steam and/or electricity via gas and/or steam turbines..

The invention is not limited by the
5 above description but can be varied within the limits of the subsequent patent claims. Thus it will be evident to the expert that the steam which is produced in the super-heated section can have a variable temperature preferably between 400°-600°C and the pressure can vary within a
10 wide range up to about 160 bar.

Additionally instead of steam the heat of the gas can be used to produce preheated air for the reactor.

The gas temperature after the boiler
can also be varied, suitably within the range 150°-300°C.
15 The gas that is taken out of the top of the separator has in the preferred case a temperature of 500°-700°C. The temperature in the reactor is suitably above 800°C and can reach up to 1500°C. A preferred range is however 800°-1300°C. Neither is the invention limited to a
20 reactor with an outlet at the lower end of the reactor, which in certain cases can create problems (in particular deposition problems) if the size of the melt particles varies widely. Thus, it can in certain cases be preferred to use a reactor with an upper outlet, preferably a
25 reactor of the Kopper-Totzek type, resulting in larger melt particles being collected in a melt bath at the bottom of the reactor and the melt particles departing from the reactor with the gas stream being guaranteed to have a relatively small and therefore a relatively
30 uniform size, and thereby to ensure that all departing particles are cooled to a temperature below the solidification temperature. As an alternative instead of a cyclone, a filter, appropriately a textile filter, can be used.

Patent Claims

1. Process for the recovery of chemicals and energy from cellulose spent liquors, preferably black liquor obtained in the sulphate cellulose process, wherein the spent liquor is introduced into a gasification reactor (1) for pyrolysis and partial incineration, wherein an energy-rich gas is formed containing particles of inorganic chemical melt, the said gas mixture is conveyed out of the reactor (1) and is concomitantly cooled by injection of a finely-divided cooling medium in conjunction with the departure from the reactor (1), the said mixture of gas and non-adhesive chemical particles is conducted from a cooling chamber (2), arranged in connection with the gasification reactor (1), where they have at least partly solidified and been converted to solid phase, so that the particles included in the gas mixture become non-adhesive, and onwards to a separating arrangement (3), preferably a cyclone, where the non-adhesive chemical particles are separated from the gas, the gas stream, which has essentially been cleaned of chemical particles, is removed via an upper connection on the separating arrangement (3) while the chemical particles are removed via a lower connection on the separating arrangement (3), and wherein a subsequent heat exchange of the separated gas is carried out from an essentially preserved temperature level, characterised in that the melt particles leaving the reactor in the gas mixture are cooled to a temperature not exceeding 700°C and that the said finely-divided cooling medium is composed of water and also that the gas is washed after the heat exchange by being conducted through a washing arrangement (5), a so-called wet scrubber (5), for washing out remaining chemicals in solid form and gas form and that the separated solidified melt particles which are removed from the bottom (31) of the separating arrangement (3) are conducted to a receptacle (6) in which the particles are dissolved, wherein at least parts

of the alkaline solution formed in this way are utilised for washing the gas in the said wet scrubber (5).

2. Process according to Claim 1, characterised in that the gas mixture before the heat exchange is cooled to a temperature which is not less than 500°C.

3. Process according to Claim 1, characterised in that the heat content of the gas after the heat exchange is obtained as superheated steam.

10 4. Process according to Claim 1, characterised in that the gasification takes place at a temperature exceeding 700°C preferably at 800°-1500°C most preferred 800°-1300°C.

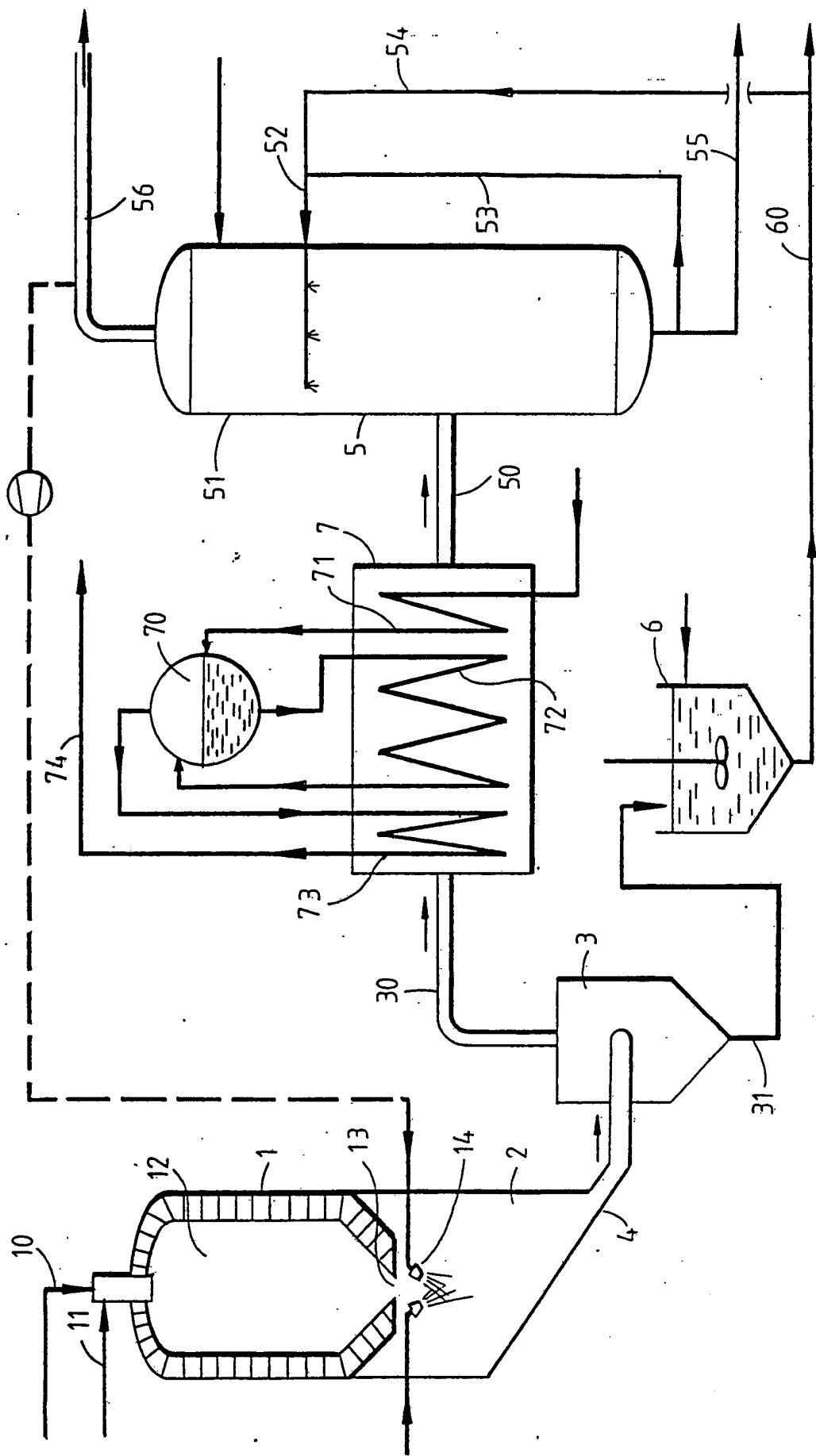
15 5. Process according to any one of the preceding claims, characterised in that the gasification takes place at atmospheric pressure.

6. Process according to any one of the preceding claims, characterised in that the gasification takes place at increased pressure.

20 7. Process according to Claim 1, characterised in that the gas at the inlet to the wet scrubber has a temperature of 100°-300°C.

8. Process according to any one of the preceding claims, characterised in that the superheated steam is conducted to a steam turbine in the condensing or back pressure procedure.

25 9. Process according to any one of the preceding claims, characterised in that the washed gas is utilised as a fuel for the production of electricity and steam in a steam turbine unit or a combined gas
30 turbine/steam turbine cycle.



INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 92/00477

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: D 21 C 11/12

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

IPC5

D 21 C

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in Fields Searched⁸

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 3073672 (K.N. CEDERQUIST) 15 January 1963, see column 3, line 30 - line 33; column 3, line 74 - column 4, line 17; column 4, line 31 - line 61; column 3, line 50 - line 54 --	1,2,4,5, 6,9
Y	US, A, 4808264 (JEAN-ERIK KIGNELL) 28 February 1989, see column 2, line 31 - line 53 --	1,2,4,5, 6,9
A	US, A, 3323858 (S.A. GUERRIERI) 6 June 1967, see column 2, line 29 - column 3, line 35 --	

* Special categories of cited documents:¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

16th October 1992

Date of Mailing of this International Search Report

21 -10- 1992

International Searching Authority

SWEDISH PATENT OFFICE

Signature of Authorized Officer

Marianne Bratsberg

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	DE, B2, 2027094 (SVENSKA CELLULOSA AB) 20 February 1975, see column 5, line 55 - line 58 -- -----	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 92/00477

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 30/09/92
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3073672	63-01-15	FR-A- 1252328	00-00-00
US-A- 4808264	89-02-28	CA-A- 1272005	90-07-31
		EP-A-B- 0223821	87-06-03
		JP-B- 3043393	91-07-02
		JP-T- 62503110	87-12-10
		SE-B-C- 448173	87-01-26
		SE-A- 8502731	86-12-04
		WO-A- 86/07396	86-12-18
US-A- 3323858	67-06-06	DE-A- 1494655	69-12-11
		FR-A- 1445181	00-00-00
DE-B2- 2027094	75-02-20	FR-A- 2049779	71-03-26
		SE-B- 363651	74-01-28